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(54) **PREPARATIONS DE POLYURETHANE EXPANSIBLES, POSSEDANT DE BONNES QUALITES D'ECOULEMENT; METHODE POUR DES MOULAGES EN POLYURETHANE EXPANSE**

(54) **FOAMABLE POLYURETHANE PREPARATIONS WHICH EXHIBIT GOOD FLOW BEHAVIOR, ANDA PROCESS FOR PRODUCING FOAMED POLYURETHANE MOLDINGS**

(57) Mélange réactionnel expansible, renfermant A) 100 % en poids d'un polyol constitué a) de 50 à 99 % en poids, pourcentage basé sur 100 % en poids de constituant A, d'huile de ricin, b) de 0,9 à 49,9 % en poids, pourcentage basé sur 100 % en poids de constituant A, d'un constituant réactif avec les isocyanates, de préférence un constituant extenseur de chaîne et (ou) réticulant, renfermant des hydroxyles réactifs, c) de 0,1 à 5 % en poids, pourcentage basé sur 100 % en poids de constituant A, d'eau et, facultativement, d) de produits auxiliaires et (ou) d'additifs, B) un isocyanate et, facultativement, C) des charges minérales et (ou) des agents de renforcement. L'invention concerne également des moulages en polyuréthane expansé, obtenus par réaction de A avec B, facultativement en présence de C); méthode pour la production d'articles moulés en polyuréthane expansé, avec ces types de mélanges.

(57) A foamable reaction mixture comprising A) 100 % by weight of a polyol component consisting of a) 50 to 99% by weight, based on 100% by weight of component A), of castor oil, b) 0.9 to 49.9% by weight, based on 100% by weight of component A), of an isocyanate-reactive component, preferably a chain extending and/or a crosslinking component containing reactive hydroxyl groups, c) 0.1 to 5% by weight, based on 100% by weight of component A), of water, and, optionally d) auxiliary materials and/or additives, B) an isocyanate component, and, optionally C) inorganic fillers and/or reinforcing agents. The present invention also relates to foamed polyurethane molding produced by reacting A) with B), optionally in the presence of C), and to a process for the production of foamed polyurethane moldings based on these foamable reaction mixtures.

FOAMABLE POLYURETHANE PREPARATIONS WHICH EXHIBIT GOOD FLOW BEHAVIOR, AND A PROCESS FOR PRODUCING FOAMED POLYURETHANE MOLDINGS

ABSTRACT OF THE DISCLOSURE

A foamable reaction mixture comprising

A) 100 % by weight of a polyol component consisting of

a) 50 to 99% by weight, based on 100% by weight of component A), of castor oil,

b) 0.9 to 49.9% by weight, based on 100% by weight of component A), of an isocyanate-reactive component, preferably a chain extending and/or a crosslinking component containing reactive hydroxyl groups,

c) 0.1 to 5% by weight, based on 100% by weight of component A), of water,

and, optionally

d) auxiliary materials and/or additives,

B) an isocyanate component,

and, optionally

C) inorganic fillers and/or reinforcing agents.

The present invention also relates to foamed polyurethane molding produced by reacting A) with B), optionally in the presence of C), and to a process for the production of foamed polyurethane moldings based on these foamable reaction mixtures.

FOAMABLE POLYURETHANE PREPARATIONS WHICH EXHIBIT GOOD FLOW BEHAVIOR, AND A PROCESS FOR PRODUCING FOAMED POLYURETHANE MOLDINGS

BACKGROUND OF THE INVENTION

The present invention describes a foamable reaction mixture which is capable of forming a foamed polyurethane molding. This foamable reaction mixture exhibits improved flow properties and the resultant foamed polyurethane moldings exhibit improved energy absorption properties. In this respect, a foamable reaction mixture is understood to be a polyol component and an isocyanate component, which are reacted, optionally with the addition of other auxiliary materials, to form a polyurethane foamed material. The present invention also describes a process for producing foamed moldings from the polyurethane system according to the invention.

The object of the present invention was to provide a foamable reaction mixture which is free from chlorofluorocarbons and which exhibits improved flow behavior. In particular, this foamable reaction mixture has an adjustable working life, which can be extremely long if desired, and polyurethane foamed moldings produced from these foamable reaction mixtures exhibit a very low heat tone and improved energy absorption properties. In addition, another object of the present invention was to provide a process for the production of polyurethane foamed moldings from the foamable reaction mixture of the invention.

Surprisingly, it has been found that the objects of the invention can be achieved by the use of a foamable reaction mixture containing castor oil.

SUMMARY OF THE INVENTION

The present invention relates to a foamable reaction mixture which comprises:

A) 100 % by weight of a polyol component comprising:

   a) 50 to 99% by weight, based on 100% by weight of component A), of castor oil,

b) 0.9 to 49.9% by weight, based on 100% by weight of component A), of an isocyanate-reactive component containing hydroxyl groups,

c) 0.1 to 5% by weight, based on 100% by weight of component A), of water,

and, optionally,

d) additives,

and

B) an isocyanate component,

and, optionally,

C) inorganic fillers and/or reinforcing agents.

It is preferred that these foamable reaction mixtures comprise:

A) 100 % by weight of a polyol component comprising:

a) 50 to 99% by weight, based on 100% by weight of component A), of castor oil,

b) 0.9 to 49.9% by weight, based on 100% by weight of component A), of an isocyanate-reactive component containing hydroxyl groups,

c) 0.1 to 5% by weight, based on 100% by weight of component A), of water,

and

d) additives comprising:

i) from 0.01 to 5 % by weight, based on 100% by weight of component A), of at least one catalyst,

and

ii) 0.01 to 5 % by weight, based on 100% by weight of component A), of cell stabilizers,

and

B) an isocyanate component,

and, optionally,

C) inorganic fillers and/or reinforcing agents.

Other additives which may optionally be included in these foamable reaction mixtures as a portion of component A)d) include, for example, mold release agents, anti-foaming agents, flame retardants, etc. The present invention also provides foamed polyurethane moldings having a density of from 10 g/l to 1100 g/l (without inorganic fillers and/or reinforcing agents), produced from a foamable reaction mixture which comprises:

A) 100 % by weight of a polyol component comprising:

a) 50 to 99% by weight, based on 100% by weight of component A), of castor oil,

b) 0.9 to 49.9% by weight, based on 100% by weight of component A), of an isocyanate-reactive component containing hydroxyl groups,

c) 0.1 to 5% by weight, based on 100% by weight of component A), of water,

and, optionally,

d) additives,

and

B) an isocyanate component,

and, optionally,

C) inorganic fillers and/or reinforcing agents.

It is preferred that component d), i.e. the additives, of this reaction mixture comprise

i) 0.01 to 5% by weight, based on 100% by weight of component A), of at least one catalyst,

ii) 0.01 to 5% by weight, based on 100% by weight of component A) of cell stabilizers.

Mold release agents and flame retardants, etc. may also be present as additives in the above reaction mixture.

The present invention also provides a process for the production of polyurethane foamed moldings, comprising reacting

A) 100 % by weight of a polyol component comprising:

a) 50 to 99% by weight, based on 100% by weight of component A), of castor oil,

b) 0.9 to 49.9% by weight, based on 100% by weight of component A), of an isocyanate-reactive component containing hydroxyl groups,

c) 0.1 to 5% by weight, based on 100% by weight of component A), of water,

and, optionally,

d) additives,

with

B) an isocyanate component,

and, optionally,

C) inorganic fillers and/or reinforcing agents.

The foamed polyurethane moldings produced from the foamable reaction mixtures of the present invention exhibit a horizontal progression of the curve in the Audi compression test.

Advantages of the polyurethane foamed moldings produced from the foamable reaction mixtures according to the invention include, for example, a very low water uptake, a high rigidity at a low density, low brittleness despite high rigidity and low density, and that very low densities can be obtained by foaming with water, without resulting in discoloration of the core of the foamed molding.

The foamable reaction mixtures and polyurethane foamed moldings produced according to the invention comprise components A) and B), and, optionally, C).

Component A) is the polyol component and comprises the individual components a) to c) as described herein, or a) to c) and d)i) and/or d)ii).

Suitable for use as component a) is castor oil of the known, commercially available degree of purity.

Suitable compounds for use as component b) include, for example, those polyols and/or polyamines which contain isocyanate-reactive groups. Such compounds fall into two areas, 1) those having relatively low molecular weights which are commonly referred to as chain extenders and/or crosslinking agents, and 2) relatively high molecular weight compounds. Castor oil (i.e. component a) above) is of course, excluded from suitable compounds for use as component b) in the present invention.

Chain extenders and/or crosslinking agents for use as component 1) of b) typically include water and those compounds having molecular weights in the range of from 60 to 1799, preferably of from 62 to 500, most preferably of from 62 to 400, which contain at least two groups capable of reacting with isocyanate groups. Some examples of suitable compounds include polyhydric alcohols such as those disclosed in, for example, U.S. Patents 4,774,263 and 4,774,264, the disclosures of which are herein incorporated by reference. The following alcohols are particularly preferred for use as component b): ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), propylene glycol (PG), dipropylene glycol (DPG), tripropylene glycol (TPG), butanediol, hexanediol. Suitable compounds also include aliphatic polyamines which contain ether groups such as, for example, polypropylene oxides of the above molecular weight range which may contain terminal primary amino groups for example, and also aliphatic polyhydroxyl compounds which contain ether groups such as, for example, addition compounds of ethylene oxide and/or propylene oxide with trimethylolpropane, pentaerythritol or ethylenediamine. Polyols which contain cycloaliphatic rings are also suitable. Some examples of these compounds containing cycloaliphatic rings include 1,4-dihydroxycyclohexane or 1,4-bis-hydroxymethyl-cyclohexane, for example, and polyamines, such as 1,4-cyclohexane diamine, isophorone diamine, bis-(4-amino-cyclohexyl)-methane or bis-(3-methyl-4-aminocyclohexyl)-methane, for example. The compounds containing hydroxyl groups are preferred over the compounds containing amine groups.

Suitable compounds having relatively high molecular weight and containing isocyanate reactive groups for use as component 2) of b) include, for example, those compounds having molecular weights in the range of from 1800 to 12,000, preferably 3000 to 7000. These compounds must also contain groups which are capable of reacting with isocyanate groups, or mixtures of compounds of this type, wherein component b)2) has an (average) functionality greater than about 2.5, preferably of 2.6 to 3.0, and most preferably of 2.8 to 3.0, which are capable of reacting with isocyanate groups in an isocyanate addition reaction. Compounds which are particularly suitable as component b) include, for example, polyether polyols or mixtures of polyether polyols which fall within the above categories. These include, for example, those compounds which are disclosed in, for example, U.S. Patent 4,218,543, the disclosure of which is herein incorporated by reference. Suitable preferred polyether polyols are described as those in which at least 50%, more preferably at least 80%, of the hydroxyl groups consist of primary hydroxyl

groups. Suitable compounds include, for example, polyesters, polythioethers, polyacetals, polycarbonates or polyester amides which contain hydroxyl groups. Examples of these compounds are disclosed in, for example, U.S. Patent 4,218,543. Such compounds are, however, less preferred than are the polyether polyols.

Other suitable substances for use as component b) include, for example, aminopolyethers or mixtures of aminopolyethers, i.e. polyethers containing groups which are capable of reacting with isocyanate groups wherein at least 50 equivalent %, preferably at least 80 equivalent % of the isocyanate reactive groups are composed of primary and/or secondary, aromatically or aliphatically, preferably aromatically bonded amino groups. The remainder of the isocyanate reactive groups of these aminopolyethers being composed of primary and/or secondary, aliphatically bonded hydroxyl groups. Examples of suitable amino-polyethers of this type are the compounds are described in, for example, U.S. Patents 4,774,263 and 4,774,264, the disclosures of which are herein incorporated by reference.

Polyesters which contain amino groups, are also suitable as starting component b)2), but are less preferred.

Any mixtures of the polyhydroxyl compounds described above as suitable examples with any of the aminopolyethers described above as suitable examples can, of course, also be used as component b)2). In the present invention, compounds having molecular weights of from 1800 to 12,000 are optionally used.

Suitable for use in the present invention as component c) is water. It is also possible to use complexes, addition compounds, inclusion compounds, etc., which release water. It is preferred, however, that free water be used.

The foamable reaction mixtures of the present invention may optionally include component d) additives. Some examples of the various auxiliary materials and/or additives which are optionally used in conjunction during the production of the polyisocyanate addition polymerization products include internal mold release agents (IMRs), catalysts for the polyisocyanate addition polymerization reaction, foaming agents, surface-active additives, cell regulators, organic and inorganic pigments, colorants, UV and thermal stabilizers, plasticizers or substances with a

fungistatic or bacteriostatic effect, such as those described in, for example, U.S. Patents 4,774,263 and 4,774,264, the disclosures of which are herein incorporated by reference.

Examples of suitable catalysts to be used as additives in the present invention include tertiary amines, tin compounds and/or organic acids such as acetic acid. Specific catalysts which fall within these broader groups of catalysts are well known in the art.

Suitable for component B), the isocyanate component of the present invention, are the aromatic polyisocyanates known in the art. These aromatic polyisocyanates have an NCO group content of 10 to 50% by weight, and include, for example, methylene diphenylene diisocyanate and toluene diisocyanate.

Other suitable isocyanates for the present invention include those isocyanates having a molecular weight higher than 137, and preferably of 168 to 290, and which exclusively contain (cyclo)aliphatically bonded isocyanate groups. Examples of such compounds include isocyanates such as 1,6-diisocyanatohexane, 1,12-diisocyanatododecane, 1,3-diisocyanatocyclobutane, 1,3- and 1,4-diisocyanato-cyclohexane and any mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanato-methylcyclohexane (IPDI) or 2,4- and/or 4,4'-diisocyanatodicyclo-hexyl-methane for example, or any mixtures of simple (cyclo)aliphatic polyiso-cyanates of this type.

In addition, polyisocyanates which are suitable include those which are modified by urethane, allophanate, isocyanurate, urea, biuret and/or uretdione groups, and which are based on the aromatic and (cyclo)-aliphatic diisocyanates cited by way of example or which are based on mixtures thereof. Mixtures of unmodified diisocyanates with the modified polyisocyanates can also be used as component B).

The foamable reaction mixtures and the foamed polyurethane moldings of the present invention may optionally comprise component C), inorganic fillers and/or reinforcing agents. Suitable for use as fillers and/or reinforcing agents in the present invention are those materials known in the art such as, for example, barium sulphate, kieselguhr, whitening, mica, and particularly glass fibers, LC fibers, glass flakes, glass spheres, or aramid or carbon fibers for example. They

are preferably incorporated in component A), the polyol component, or in the case of continuous reinforcing materials they may also be inserted into the mold. Materials can also be used which are employed in order to reduce the bulk density, such as, for example, pumice stone or other synthetic or naturally occurring inorganic materials of low density.

Foamable reaction mixtures of the present invention which are slow reacting mixtures can be processed by manual means. It is preferred to use mechanical mixing and/or mechanical loading of molds when the foamable reaction mixtures of the present invention are fast reacting mixtures, or more rapid than can be manually mixed effectively. The processing of foamable reaction mixtures and foamed polyurethane molding is known. The details can be found in, for example, G. Oertel (editor), Polyurethane, Hanser-Verlag, Munich, 3rd Edition, 1993.

The molding compositions of the present invention can be used, for example, in the construction and leisure industries for filling any hollow cavities or hollow chamber sections with foam. These can also be used in the automobile industry for the production of energy-absorbing foamed materials.

The following examples further illustrate details for the process of this invention. The invention, which is set forth in the foregoing disclosure, is not to be limited either in spirit or scope by these examples. Those skilled in the art will readily understand that known variations of the conditions of the following procedures can be used. Unless otherwise noted, all temperatures are degrees Celsius and all percentages are percentages by weight.

EXAMPLES

The following components were used in the examples:

POLYOL 1: a crosslinking agent having an OH number of 1000, and being produced by the addition of propylene oxide to trimethylolpropane.

ISO 1: polymeric diphenylmethane polyisocyanate (commercially available as Desmodur 44V20 from Bayer) having an NCO group content of 31.5% by weight.

CAT 1: acetic acid

CAT 2: a tertiary amine catalyst, commercially available as Dabco 33LV from Air Products .

STAB 1: cell stabilizer based on polysiloxane, commercially available as SR 242 from Goldschmidt.

Example 1

A foamable reaction mixture was formed which comprised the following polyol component A), and isocyanate component B).

Polyol formulation (OH number = 516 mg KOH/g):

castor oil	77 parts
POLYOL 1	4 parts
diethylene glycol	16 parts
STAB 1	1 part
water	3 parts
CAT 1	0.1 part
CAT 2	1 part

The above polyol component was mixed with ISO 1, having an NCO group content of 31.5% to form the foamable reaction mixtures of the present

application. The quantity of ISO 1 added was sufficient to provide an isocyanate index of 110.

Processing characteristics:

Start Time:	15 seconds
rise time:	25 seconds
curing time[1]:	22 seconds
mold material	aluminum
mold release agent	wax
mold temperature	25°C
Bulk density (g/l)	55 g/l

[1]: time to become stringy

Mechanical properties of a foamed polyurethane molding produced from the above reaction mixture:

compressive hardness (70 % compressive deformation): 94 kPa.

Example 2:

A foamable reaction mixture was formed which comprised the following polyol component A), and isocyanate component B).

Polyol formulation (OH number = 406 mg KOH/g):

castor oil	77 parts
POLYOL 1	4 parts
diethylene glycol	16 parts
STAB 1	1 part
water	1 part

The above polyol component was mixed with ISO 1, having an NCO group content of 31.5% to form the foamable reaction mixtures of the present application. The quantity of ISO 1 added was sufficient to provide an isocyanate index of 110.

Processing characteristics:

start time	285 seconds
rise time	about 20 mins.
curing time[1]	about 15 mins.
mold material	aluminum
mold release agent	wax
mold temperature	25°C
Bulk density (g/l)	150 g/l

[1]: time to become stringy

Mechanical properties of a foamed polyurethane molding produced from the above reaction mixture:

compressive hardness (70 % compressive deformation): 1162 kPa.

This formulation was capable of flowing over extended flow paths of several meters, even with low wall thicknesses, and foamed extremely uniformly. The cell structure, the uniformity of the cells and the density were completely identical over a vertically upward flow path of 3 meters, for example.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A foamable reaction mixture comprising:

A) 100% by weight of a polyol component comprising:

1) 50 to 99% by weight, based on 100% by weight of component A), of castor oil,

2) 0.9 to 49.9% by weight, based on 100% by weight of component A), of an isocyanate-reactive component containing hydroxyl groups,

3) 0.1 to 5% by weight, based on 100% by weight of component A), of water,

and, optionally,

4) additives,

B) an isocyanate component,

and, optionally,

C) inorganic fillers and/or reinforcing agents.

2. The foamable reaction mixture of Claim 1, wherein:

A) said polyol component comprises:

1) 50 to 98.98% by weight, based on 100% by weight of component A), of castor oil,

2) 0.9 to 49.88% by weight, based on 100% by weight of component A), of an isocyanate-reactive component containing hydroxyl groups,

3) 0.1 to 5% by weight, based on 100% by weight of component A), of water,

and

4) additives comprising:

i) from 0.01 to 5% by weight, based on 100% by weight of component A), of catalysts,

and

ii) 0.01 to 5% by weight, based on 100% by weight of component A) of cell stabilizers;

B) an isocyanate component,

and, optionally,

C) inorganic fillers and.or reinforcing agents.

3. A foamed polyurethane molding having a density of 10 g/l to 1100g/l, and comprising the reaction product of

A) 100% by weight of a polyol component comprising:

1) 50 to 99% by weight, based on 100% by weight of component A), of castor oil,

2) 0.9 to 49.9% by weight, based on 100% by weight of component A), of an isocyanate-reactive component containing hydroxyl groups,

3) 0.1 to 5% by weight, based on 100% by weight of component A), of water,

and, optionally,

4) additives,

B) an isocyanate component,

and, optionally,

C) inorganic fillers and/or reinforcing agents.

4. The foamed polyurethane molding of Claim 3, wherein

A) said polyol component comprises:

1) from 70 to 95% by weight, based on 100% by weight of component A), of castor oil.

5. The foamed polyurethane molding of Claim 4, wherein:

A) said polyol component comprises:

1) 80 to 90% by weight, based on 100% by weight of component A), of castor oil.

6. A process for the production of foamed polyurethane moldings, comprising reacting:

A) 100% by weight of a polyol component comprising:

1) 50 to 99% by weight, based on 100% by weight of component A), of castor oil,

2) 0.9 to 49.9% by weight, based on 100% by weight of component A), of an isocyanate-reactive component containing hydroxyl groups,

3) 0.1 to 5% by weight, based on 100% by weight of component A), of water,

and, optionally,

4) additives,

with

B) an isocyanate component,

and, optionally,

C) inorganic fillers and/or reinforcing agents.